

Final/Annual/Midterm Report for AOARD Grant
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**"Development and Exploration of Nanoparticle Decorated Carbon Supports
(Graphene and Graphene Oxide) for Energy Collection, Storage, and Conversion"**

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1. Abstract:

Solution-processible graphene, produced by the chemical exfoliation of graphite, represents a new class of polyaromatic carbon materials that can have superior electrical conduction properties compared to organic materials. Graphene with high surface areas can serve as supports for metal nanoparticles and form an integral component of energy storage or conversion devices such as fuel cells, batteries or photoelectric cells. The surface chemistry and structure of the catalyst support significantly influence its dispersion and their durability. Our motivation for this work is two-fold. Firstly, we researched on the chemical methods to coat graphene with inorganic nanoparticles. A one-pot synthesis method was used to produce a wide range of metal nanoparticle-decorated (Pt, Au, Ag, Pt/Ru) graphene oxide (GO) hybrids as well as inorganic particle-graphene ($TiO_2/PbSe/G$) hybrids. These hybrids were then evaluated for their performance in energy conversion devices and two examples were chosen, namely stacked fuel cells as well as photodetector devices. We demonstrated that reduced graphene oxide (rGO) had the potential to supersede the conventional carbon black as catalyst support due to its excellent electrocatalytic performance. Besides exploring the use of GO as catalyst support, electrochemically exfoliated few-layer graphene flakes were employed as charge collection and dispersion matrix in a hybrid photoconductive film.

2. Background and motivations

2.1 PEM fuel cells and its supports

PEM fuel cells can be categorized as methanol- or hydrogen-based depending on the fuel used for the energy conversion. Hydrogen fuel cell utilizes hydrogen as fuel and the working principle can be briefly understood as oxidation of hydrogen (H_2) gas into protons at anode and reduction of oxygen (O_2) gas at cathode to generate water. Electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity. Platinum (Pt) or platinum-based alloy nanoparticles are essentially effective catalysts in fuel cell technologies. The advantage of Pt-based catalysts is that they afford low over-potential in H_2 oxidation which facilitates high catalytic efficiency especially in PEM fuel cells. That said, however, such catalysts still necessitate very high fabrication cost (Gong et al., 2009) owing to their obvious high market prices and limited availability. Therefore, the holy grail of fuel cell technology is to replace the noble Pt with non-noble (and cheaper) metal or reduce the loading of Pt in Pt-based alloy catalysts. To date, however, Pt is still regarded as the best electrocatalyst in fuel conversion and widely researched worldwide due to its small

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14. ABSTRACT Solution-processible graphene, produced by the chemical exfoliation of graphite, represents a new class of polyaromatic carbon materials that can have superior electrical conduction properties compared to organic materials. Graphene with high surface areas can serve as supports for metal nanoparticles and form an integral component of energy storage or conversion devices such as fuel cells, batteries or photoelectric cells. The surface chemistry and structure of the catalyst support significantly influence its dispersion and their durability. Our motivation for this work is two-fold. Firstly, we researched on the chemical methods to coat graphene with inorganic nanoparticles. A one-pot synthesis method was used to produce a wide range of metal nanoparticle-decorated (Pt, Au, Ag, Pt/Ru) graphene oxide (GO) hybrids as well as inorganic particle-graphene (TiO₂/PbSe/G) hybrids. These hybrids were then evaluated for their performance in energy conversion devices and two examples were chosen, namely stacked fuel cells as well as photodetector devices. We demonstrated that reduced graphene oxide (rGO) had the potential to supersede the conventional carbon black as catalyst support due to its excellent electrocatalytic performance. Besides exploring the use of GO as catalyst support, electrochemically exfoliated few-layer graphene flakes were employed as charge collection and dispersion matrix in a hybrid photoconductive film.		
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over-potential. To ensure high activity for fuel cell reaction, this active surface area of Pt sites is particularly important as it is directly influenced by the nature of catalyst support. Without the presence of an appropriate support platform, Pt nanoparticles tend to agglomerate and this essentially reduces the electrocatalytic efficiency.

An ideal carbon support for PEMFC electrocatalysts is one that integrates good electrical conductivity with high surface area and a pore structure that allows for filling of ionomer or polymer electrolyte to bring the catalyst particles close to the reactants and thus maximize the three-phase interface (electrode-electrolyte-reactant) (Dicks, A.L., 2006). In this work, we have investigated the use of GO as support for Pt catalysts and the different processing methods of GO were evaluated to study the correlation between physical properties and energy conversion efficiencies.

2.2 Solution-processible photodetector based on graphene-TiO₂-PbSe hybrid films

High performance, solution-processible infrared (IR) photodetectors are of great interest due to its amenability to low cost mass production. The use of size-tunable quantum dots such as PbSe in IR photodetector is attractive because of their high extinction coefficient, large intrinsic dipole moment and compatibility with solution processable techniques in manufacturing. Hybrid inorganic-organic photoconductor film with improved performance over PbSe-only film can be made by blending the colloidal nanocrystals in a matrix of conducting polymer derivatives, where the nanocrystals act as electron acceptors and the polymer as hole transporters. However the hole transporting property of the organic matrix is often poor, leading to limited device performance. In lieu of the organic matrix, graphene can play the dual role of ambipolar transporter and dispersal platform for the nanocrystals. Considering that the charge mobility in nanocrystalline films is limited by grain boundaries, the presence of graphene sheets in the inorganic matrix provides alternative conducting channel for charge collection. Coupling quantum dots (QD) to the π-conjugated network on graphene potentially allows the excitonic state of the QD to be transformed into a charge transfer state, and the charge injection to graphene is expected to occur at a timescale faster than exciton recombination. Thus in this work, we investigate the multiphase assembly of TiO₂ and PbSe nanocrystals on the graphene platform which allows the synergistic effects of these nanocrystals for the broadband photocurrent conversion to be explored. In the layered architecture, the photoconductor response arises from efficient electron injection from the photoexcited PbSe QD to TiO₂ or graphene.^[12] Different from conventional approaches where hydrophilic GO derivatives are employed in composites due to its solution-processibility, we apply exfoliated few-layer graphene (FLG) flakes as the matrix for direct interfacing to these nanocrystals. The advantages of using FLG include its higher electrical conductivity compared to GO, which will improve the efficiency of charge collection.

3. Experimental

3.1 GO-Pt fuel cell

Synthesis of graphene-Pt hybrid

Graphene (reduced graphene oxide (r-GO), Base-acid washed GO (BAGO) and Exfoliated graphene (EG)) was used as starting material. The graphene was dispersed in propylene glycol and sonicated for 1 hour until homogenous dispersion was obtained. Graphene dispersion in propylene glycol was bubbled under nitrogen atmosphere for 15 minutes to purge the trapped oxygen. The dispersion was heated under reflux with magnetic stirring under exposure of nitrogen. Then, the metal precursor was rapidly injected into the hot dispersion at 150 °C and heating continues for 1 hour. The hot dispersion was cooled in ice-bath. The graphene-Pt hybrid was separated from propylene glycol solution by centrifuging at 8000 rpm and precipitate is repeatedly washed with water and ethanol, respectively. The hybrid was dried in oven overnight.

Fuel cell testing

To examine the performance of the fuel cell, a single stack fuel cell was assembled (and customized). It was fabricated using a membrane/electrode assembly consisting two stainless steel plates with flow manifolds on the supply sides for gas and water and two Teflon gaskets. The anode was a 5 cm^2 20% Pt/C Johnson Matthey electrode (JM), rGO-Pt, BAGO-Pt, EG-Pt, respectively, with a platinum loading of 0.4 mg cm^{-2} . The cathode was prepared from a suspension containing 0.0181 g (70%) of catalyst, 0.155 g (30%) of 5 wt% Nafion recast solution and 0.5 ml of distilled H_2O and had been ultrasonically-blended for 1 hour. The suspension was spread evenly across the surface of a carbon paper substrate (Toray TGPH-090). A single cell assembly was produced by sandwiching a Nafion 1135 membrane (Du Pont) between the anode and cathode.

3.2 Graphene-Inorganic hybrids for photodector applications

Graphene Synthesis. The electrochemical exfoliation of few layer graphene (FLG) from graphite powder was carried out according to our previously reported method.^[13] Briefly, graphite powder was negatively charged (cathode) and a carbon rod was used as the positive electrode (anode) in an electrochemical cell. Graphite powder (100 mg) was packed in a porous plastic tube, an Al electrode was inserted inside and negatively charged in 100 ml of nearly saturated solution of LiClO_4 in propylene carbonate (PC) using a voltage of 10V. During the charging, HCl/DMF solution was used to remove solid byproducts. After that, the expanded graphite was transferred into a glass Suslick cell (30 ml) with saturated LiCl in a mixture of DMF solution (10 ml), PC (2 ml) and TMA (1 ml). Next, the dispersion was sonicated for >10 hours (5h+5h) (70% amplitude modulation, Sonic s VCX750, 20 kHz). The sonicated graphene powder was washed by HCl and water and ethanol, respectively. The black graphene powder was collected by centrifugation during the washing. The above process was repeated two times to improve the yield of FLG.

PbSe/graphene heterostructure. The synthesis was all carried out in argon atmosphere. Two stock solutions of Pb-oleate and TOP-Se were separately prepared in advance. PbO (450 mg) in oleic acid (2.0 ml) and Se (150 mg) in TOP (1.5 ml) was separately heated to get a clear solution at 120°C under argon flow. 15 ml ODE was added into the PbO -oleate solution in three neck flask. Graphene (3 mg) in diphenyl ether (15 ml) was sonicated (60% amplitude) for 5 min and then immediately added to the PbO -oleate-ODE solution. When the solution was heated to $160\text{-}170^\circ\text{C}$, TOP-Se solution was rapidly injected into the hot dispersion. The nanocrystal growth time was controlled for 5-7 min, then the reaction mixture was cooled down and acetone added. The PbSe/graphene was purified by precipitation with hexane/acetone, hexane/isopropanol and pyridine, respectively (each twice).

PbSe/graphene/TiO₂ hybrids. 3 ml of clear $\text{Ti(O-i-C}_4\text{H}_9)_4$ was injected into 100 ml of 0.1 mg/ml of FLG/PbSe dispersed in iso-propanol (IPA) under Ar gas bubbling. The stabilizer of FLG/PbSe flakes was exchanged with pyridine. The mixture was refluxed for several hours in oil bath (90°C). Then, 10 ml of IPA with the adding of one drop ($\sim 0.25\text{ ml}$) H_2O before was dropped into the above mixture with strong stirring and the refluxing was supported overnight. After that the mixture was centrifuged at 1500 rpm and the precipitate was washed by IPA for 5 times. Finally the FLG/PbSe//TiO₂ was dispersed in IPA for film spin casting.

Photodetector device fabrication. All photoconductor systems PbSe, FLG/PbSe and FLG/PbSe/TiO₂ were dispersed in DCB and spin casted (600 rpm, 60sec) on pre-cleaned ITO substrates. The thickness of the photoactive layers is about 100nm. The spin-casted photoactive layers were annealed to 160°C for 10 min, this is followed by thermal eva

poration of Al cathode to complete the photodetector device fabrication.

4. Results and discussion

4.1 Characterization of graphene-Pt hybrid

We employed a generic one-pot synthesis method to coat a wide range of nanometal on graphene platform. Glycol solvent (ethylene glycol or propylene glycol) was used as dispersing medium for graphene flakes and simultaneously acted as reducing agent to reduce the metal precursor to metal nanoparticles. Butylamine was added as a binder to immobilize the crystal growth of the nanometal on graphene flakes. The method allows elegant control of nanometal phase, density and size. The uniqueness of this generic method is reflected by the uniform coating of a wide range of metals such as Au, Ag, Pt, Pt-Ru on graphene flakes as shown in Figure 1.

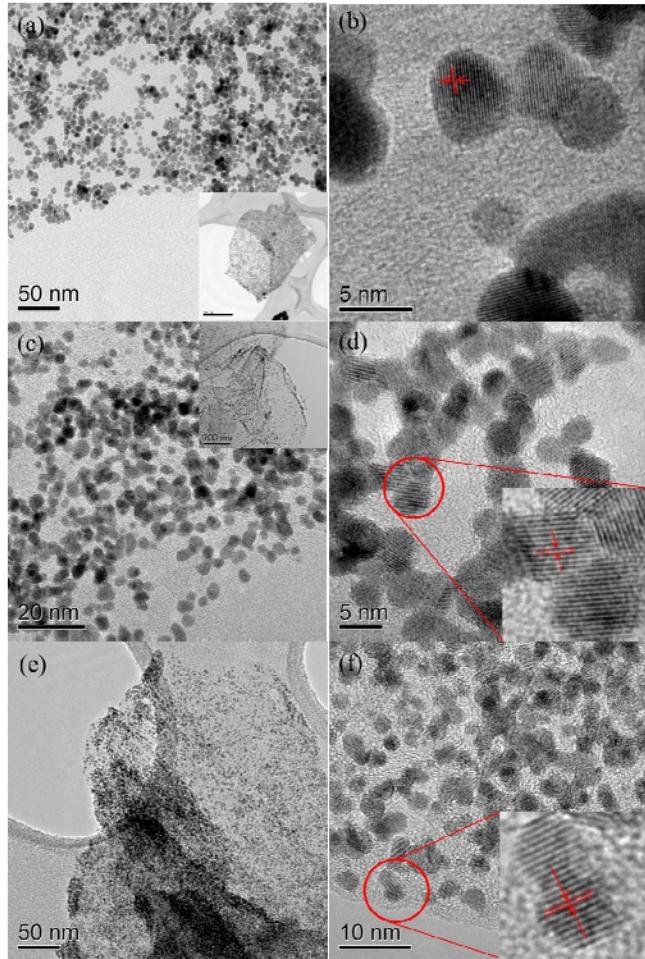


Figure 1. TEM images of platinum nanoparticles coating different type of graphene, including (a,b) Pt on exfoliated graphene (c,d) Pt on reduced GO (e,f) Pt on base and acid-washed GO.

4.2 Single stack fuel cell performance

The applicability of Pt/rGO hybrids as fuel cell catalyst in real working environments was reflected by the performance in single stack PEM fuel cell. Pt/rGO hybrids (0.4 mg/cm^2) were loaded on carbon cloth as anode and the standard Pt/C(JM) as cathode. Proton membrane assemblies were constructed and tested at different temperatures.

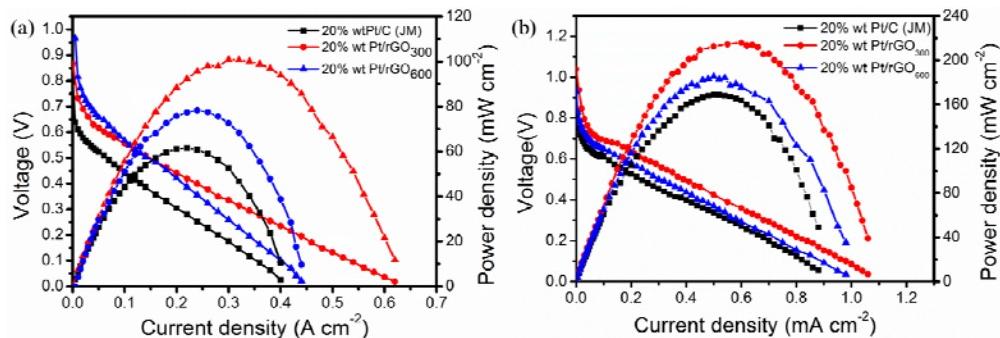


Figure 2. Polarization curves of a single stack PEM fuel cell using Pt/rGO300, Pt/rGO600 and commercial Pt/C (JM), respectively, as the anode catalyst in (a) 30°C and (b) 80°C .

Table 1. Performance of Pt/rGO300, Pt/rGO600 and commercial Pt/C (JM) as anode.

Catalyst	Power density (mW cm^{-2})	
	30°C	80°C
Pt/rGO300	101	216
Pt/rGO600	78	184
Pt/C (JM)	61	169

The hydrogen fuel cell performances were compared in Figure 2 and Table 1. Pt/RGO300 refers to Pt nanoparticle-decorated GO which has been thermally annealed at 300 deg C , while Pt/rGO600 refers to the same which has been thermally annealed at 600 deg C . Pt/C refers to Pt coated on conventional carbon black. It can be seen that the output voltage and power density increase as working temperature increases from 30 to 80°C . It is evident that the power densities delivered by Pt/rGO300 are the highest among the three. These performance results are in good agreement with the electrochemical surface area of rGO300 as revealed by the Cyclic voltammetry measurements, confirming that the higher surface areas and larger pore volumes afford a higher degree of catalyst dispersion while these highly integrated interconnected pore systems increases the triple-phase boundaries (electrode, electrolyte, reactant-H₂ gas).

4.3 High-Performance Broadband Photodetector Using Solution-Processible PbSe-TiO₂-Graphene Hybrids

Solution-processible photodetector array (Figure 3) is realized on the basis of a triple junction graphene-PbSe-TiO₂ hybrid system. When irradiated by 1000 nm light (intensity 2.34mW/cm²) and biased at -1V, the device exhibits high photodetection efficiency with a responsivity of 0.13 A W⁻¹, detectivity of 10¹²-10¹³ Jones (cmH^{1/2}/W) and a rise time of ~750 ns. Absorption, charge transfer and transport mechanism of the graphene/nanocrystals hybrid film were studied using transient photocurrent and photothermal deflection spectroscopy. The triple junction G-PbSe-TiO₂ system allows synergistic effects in light detection, photocarrier generation and collection and shows markedly improved photodetection efficiency compared to G-PbSe or PbSe-only system. A key process in the functioning of such devices is the dispersive transport of electrons through the network of interconnected semiconductor nanoparticles. The good electronic coupling of PbSe with G, as well as TiO₂ with PbSe, ensures efficient charge injection of photocarriers into G and/or TiO₂. We demonstrate that the exfoliated graphene flakes afford efficient charge extraction and transport in the dispersed heterojunctions. These results point to the possibilities of using multiphase assembled graphene-nanocrystal hybrid films as an alternative to organic-based photoactive materials in flexible photodetectors and solar cells.

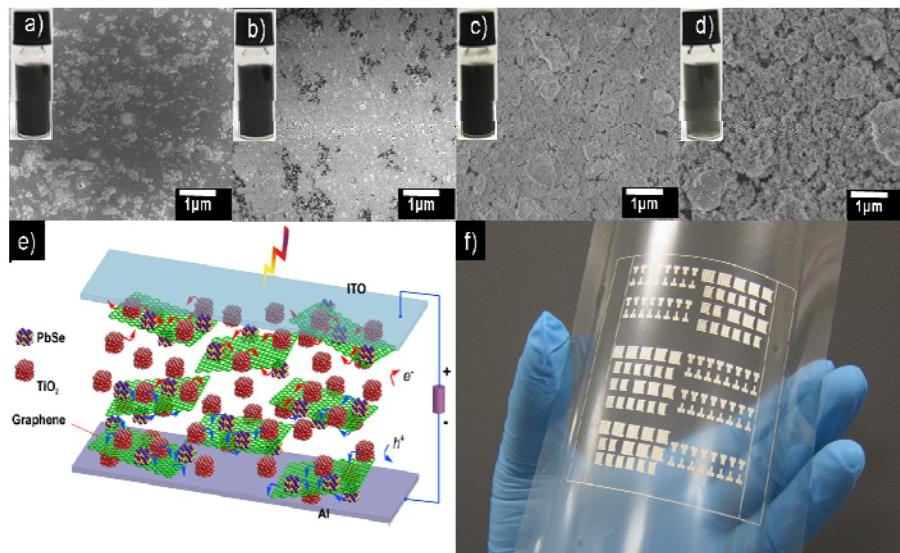


Figure 3. Solution-processable and large-area printability. SEM images of a) pure graphene b) pure PbSe c) FLG/PbSe and d) FLG/PbSe/TiO₂ films. Inset shows the corresponding dispersions. e) Schematic representation of multiphase assembly of the FLG/PbSe/TiO₂ photodetector. Arrows in red and blue shows the bias driven transport of photo generated charge carriers through conducting graphene networks. f) Large area printed FLG/PbSe/TiO₂ photodetector patterns on flexible substrate. (Note: PbSe= lead selenide; FLG = few layer graphene; TiO₂ = titanium oxide)

5. Conclusions

We have shown the feasibility of a graphene-nanometal hybrid synthesis technique which is generic to a wider range of metals and a series of graphene derivatives. Loading of Pt nanoparticles on the defective surface of reduced graphene oxide greatly enhances the fuel cell performance over that of commercial carbon black. Defect engineering on graphene sheets to further improve the fuel cell performance is a worthwhile subject to be explored moving graphene-nanometals much closer to real technological applications.

We have also developed a solution-processible photodetector which consists of a multi-component graphene-PbSe-TiO₂ hybrid system. As opposed to the more commonly used but insulating graphene oxide derivatives, we applied exfoliated few layer graphene (FLG) as part of an energy exchange matrix. The multi-component FLG/PbSe/TiO₂ system allows synergistic effects in light detection, photocarrier generation and collection and shows markedly improved photodetection efficiency compared to FLG/PbSe or PbSe-only system. These results point to the possibilities of using multiphase-assembled graphene-nanocrystal films as an alternative to organic-based photoactive materials in flexible photodetectors and solar cells.

List of Publications and Significant Collaborations that resulted from your AOARD supported project:

1. High-Performance Broadband Photodetector Using Solution-Processible PbSe-TiO₂ –Graphene Hybrids, Kiran Kumar Manga, Kian Ping Loh et. al. *Advanced Functional Material*, 24, 1697-1702 (2012)
2. The use of reduced graphene oxide as electrode materials in stacked fuel cells (manuscript in preparation).

DD882: We have no invention disclosure at this stage